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The followup of the embrittlement of nuclear power reactor pressure vessels (RPVs) is of critical importance for the safety assessment in the nuclear industry. The prediction of their future degradation is based on the extrapolation of the past testing of surveillance materials irradiated in the power reactor and in material testing reactors with accelerated dose rates. Using positron annihilation spectroscopy, however, we here reveal a kinetics of irradiation-induced precipitation, i.e., very low dose rate can significantly enhance Cu nanoprecipitation. The mechanism results in the embrittlement in practical RPVs, occurring at a much earlier stage than that found from accelerated tests, suggesting that accelerated tests are not enough for prediction of the embrittlement from Cu nanoprecipitation. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2159091]

The nuclear reactor pressure vessel (RPV) is a hard-to-replace component serving as a high-temperature and high pressure primary coolant boundary in nuclear reactors. The microscopic mechanisms of irradiation-induced embrittlement of RPV steels have been studied extensively[1–10] because the structural integrity of the vessel is essential for safety reasons. The prediction of the RPV material degradation is usually based on the extrapolation of the past testing of surveillance material irradiated in the power reactor. The results of accelerated tests in material testing reactors (MTRs)—where the irradiation dose rate is typically more than two orders of magnitude higher than that occurring in commercial power reactor RPVs—are often used to validate the prediction of the future embrittlement of the RPV material. This is indeed the only possibility to practically simulate the effects of the low dose-rate irradiation in power reactors over their lifetime (about 40 years or longer). However, a question as to how the difference in the irradiation dose-rate might affect the mechanisms of embrittlement still remains open. In particular, although the possibility that the Cu precipitation is enhanced in very low dose-rate irradiations has been pointed out,[11–15] no clear evidence for enhanced Cu precipitation, accompanied with a corresponding change in mechanical properties, has been reported.

In this work, we investigate the microscopic mechanisms of embrittlement for the RPV surveillance test specimens[16] of a Calder Hall-type reactor in Japan, and the *same* RPV material irradiated in the Japan Materials Testing Reactor (JMTR). We employ the surveillance specimens from a Calder Hall-type reactor because it gives the lowest irradiation dose-rate among all the types of power reactors; we can expect that the significant difference, about *four* orders of magnitude as mentioned below, in the dose-rate between the surveillance and the accelerated test specimens can highlight the role of the dose rate in the embrittlement mechanisms and corresponding changes in mechanical properties.

The RPV specimens used in this study are made of aluminium-killed C–Mn steel. Their chemical composition is listed in Table I. The surveillance specimens were situated inside the standpipe shell of the RPV above the core during 20 years in operation. The fast neutron irradiation dose rate for the surveillance specimens in the power reactor was 4.2×10^{8} n/cm^2 s, while that for the specimens irradiated in JMTR was 3.6×10^{12} n/cm^2 s. Although the integrated fluence was one order of magnitude larger in JMTR when compared to the power reactor (to obtain almost the same yield strength, see Fig. 1), the JMTR irradiation is almost four orders of magnitude accelerated in dose rate. The irradiation temperature of the test specimens in JMTR (220 °C) is close to the temperature of the surveillance specimens (240 °C). This small temperature difference cannot be responsible for the difference in the damage mechanisms seen in the positron annihilation experiments.

Figure 1 shows the irradiation-induced increase in yield strength, usually a good measure of the embrittlement. The strengthening is clearly observed for the specimens irradiated in JMTR (closed circles) at doses higher than 10^{18} n/cm^2. On the other hand, similar strengthening occurs after irradiation at one-order lower dose (10^{17} n/cm^2) for the power reactor surveillance specimens (open circles). We will show, using the positron annihilation technique, that this difference is due to enhanced precipitation of the Cu impurities (between 0.14–0.19 wt %; see Table I) during the low dose rate irradiation of the power reactor operation.

The positron annihilation technique has been widely accepted as a sensitive tool to detect vacancy-type defects in materials and to estimate the size of the defects by measuring positron lifetimes.[17–20] Recently, we found a "*quantum-dot*" positron state confined in nanoprecipitates embedded in materials.[21,22] This state enables us to detect Cu (sub)nanoprecipitates in steels and to reveal their atomic structure. These precipitates are less than a few nm in size and cannot

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TABLE I. Chemical composition of aluminium-killed C–Mn steel. Postweld heat treatment was conducted at 600 °C for 4 h.

C	Si	M	P	S	Ni	Cr	Cu	Mo	Al	N
0.10	0.23	1.1	0.014	0.015	0.17	0.096	0.14–0.19	0.054	0.027	0.0060

be observed even by state-of-the-art high-resolution transmission electron microscopes. The coincidence Doppler broadening (CDB) of the positron annihilation technique is the key to observe the embedded nanoprecipitates.[23,24]

A CDB spectrum is characterized by its high/low momentum component fractions, which are defined as the ratios of the high momentum $(18\times10^{-3}m_0c<p_L<30\times10^{-3}m_0c)$ and low momentum $(0<p_L<4\times10^{-3}m_0c)$ regions in the CDB spectrum to the total region, respectively.[21] For this reason, we present in Fig. 2, the high/low momentum fractions (L, H) of CDB spectra for the surveillance specimen irradiated up to a dose of 2.7×10^{17} n/cm^2 (the red arrow in Fig. 1), during about 20 years in-service irradiation, and the specimen irradiated in JMTR to a dose of 2.2×10^{18} n/cm^2 (the blue arrow in Fig. 1). The specimen of JMTR irradiation has almost the same strengthening as the surveillance specimen as shown in Fig. 1. We also plot the (L, H) point for the unirradiated RPV steel, well-annealed pure Fe and pure Cu (denoted bulk Fe and bulk Cu, respectively), and neutron-irradiated pure Fe as reference points.

If positrons are trapped at vacancy-type defects, the (L, H) point lies along a line between the points for bulk Fe (well-annealed pure Fe) and neutron-irradiated pure Fe. On the other hand, if positrons are trapped at Cu nanoprecipitates, the point lies along a line between the points for bulk Fe and bulk Cu.[9,25] Indeed, the (L, H) point for the surveillance specimen lies along a line connecting the points for bulk Fe and bulk Cu. This evidences shows quantum-confined positrons within Cu nanoprecipitates[9] and thus the formation of Cu nanoprecipitates by neutron irradiation[21] at a dose as low as 2.7×10^{17} n/cm^2 in the RPV steel irradiated in the power reactor. The positron annihilation fraction with Cu electrons[26] is estimated to be about 70% from the height of the broad peak in the CDB ratio spectrum. Taking account of the enhancement effect of the positron wave function around Cu atoms,[27] the Cu concentration in the Cu nanoprecipitates is estimated to be higher than 50%. The number density of the Cu nanoprecipitates responsible for the strengthening shown in Fig. 1 is roughly estimated[21] to be more than 10^{17} cm^{-3}. The positron lifetime spectrum shows only one lifetime component of 120 ps, close to that of bulk Fe or Cu (see Table II). This shows that vacancy-type defects or dislocation loops, and thus matrix defects, induced by the irradiation are much less than the Cu nanoprecipitates. Furthermore, the Cu nanoprecipitates are defect free, coherent with the Fe matrix.[21]

Generally, three origins have been proposed for RPV embrittlement: (i) The Cu-rich precipitates, (ii) matrix defects which are considered to be vacancy clusters (nanovoids) and/or interstitial-type dislocation loops, and (iii) intergranular segregation of P impurity atoms.[2,3] An Auger spectroscopy experiment on the irradiated surveillance specimens confirms no irradiation-induced P segregation.[28] Therefore, the above results show that embrittlement of the RPV steel irradiated in the Calder Hall reactor is due to enhanced Cu nanoprecipitation.

Contrary to the Cu nanoprecipitation in the surveillance specimen, the (L, H) point for the specimen irradiated in JMTR lies along a line between the points for bulk Fe and the irradiated pure Fe, showing that positrons are trapped at vacancy-type defects, but not at Cu nanoprecipitates.[9] The

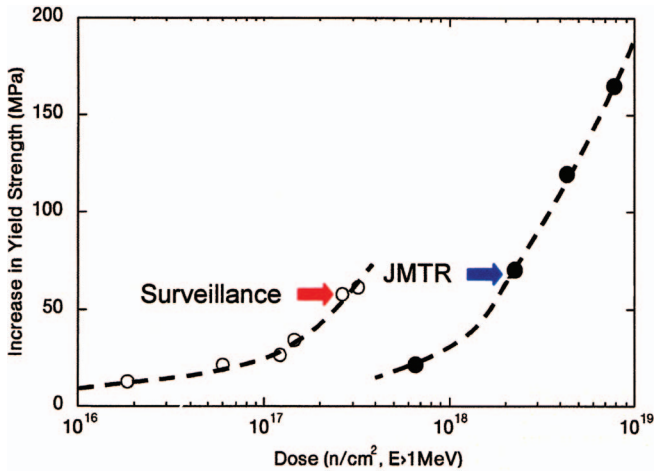

FIG. 1. (Color) Irradiation-induced increase in yield strength. Data for the surveillance test specimens (open circles) and the specimens irradiated with JMTR (closed circles) are displayed. The irradiation flux for the former is 4.2×10^8 n/cm^2 s, and that for the latter is 3.6×10^{12} n/cm^2 s. The specimens employed for positron annihilation experiments are indicated by red and blue arrows, respectively. The dashed lines are purely a guide for the eyes.

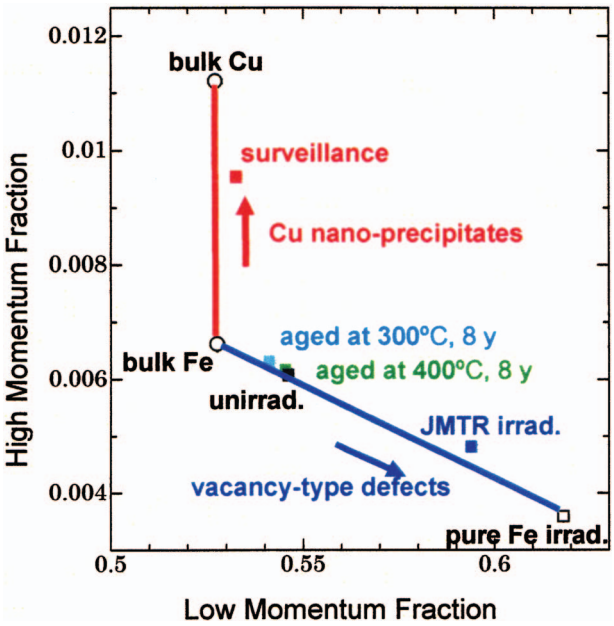

FIG. 2. (Color) High/low momentum fractions (L, H) points of CDB spectra for the surveillance test specimen, the specimen irradiated in JMTR, and thermally aged (unirradiated) RPV steels. The (L, H) points for the unirradiated RPV steel, well-annealed pure Fe and pure Cu (denoted by bulk Fe and bulk Cu, respectively), and neutron-irradiated pure Fe are also plotted as reference points.

TABLE II. Positron lifetimes of the surveillance test specimen, the specimen irradiated in JMTR, and the well-annealed pure Fe and pure Cu (denoted by bulk Fe and bulk Cu, respectively).

Surveillance	JMTR irradiated		Bulk Fe	Bulk Cu
	20 ps	176 ps		
120 ps	18%	82%	107 ps	109 ps
(1 component)	(2 components)		(1 component)	(1 component)

positron lifetime spectrum is decomposed into two lifetime components: The longer one of 176 ps with a relative intensity of 82% and the shorter one of 20 ps (see Table II). The value of 176 ps corresponds to the positron lifetime in a monovacancy.[20,29] Because monovacancies in Fe are mobile around 200 K,[30] they can only survive by binding with solute atoms or as dislocation loops. Therefore, the embrittlement in the early stage of the accelerated (high dose-rate) irradiation in the MTR is not due to the Cu nanoprecipitates but due to the matrix defects, such as vacancy-solute complexes and/or dislocation loops. This marked difference clearly shows the different mechanisms for the strengthening by the low and high dose rate irradiation.

It should be noted that Cu nanoprecipitation is only present after long-term low dose-rate irradiation, but completely absent for ageing without irradiation. To show this, we measured the CDB spectra for the same steels after thermal aging without irradiation of 8 years at 300 and 400 °C, respectively. The (L, H) points for these specimens are shown in Fig. 2. The thermal ageing effect should be enhanced when compared with the surveillance specimens because the ageing temperatures are sufficiently higher than the irradiation temperature (240 °C) of the surveillance specimens. However, the (L, H) points are very close to that for the unirradiated RPV steel, indicating no Cu nanoprecipitation. Thus, the Cu nanoprecipitation in the surveillance specimen must be enhanced even by the small amount of excess or athermal vacancies induced by the low dose-rate irradiation. Due to the self-annealing effect during the long-term irradiation (20 years), the vacancy concentration is too low to be observed by positron annihilation (lower than 10^{-7} in atomic fraction). The effects of other (non-Cu) solute/impurity elements, such as Mn, Ni, Si, and P, are not observed clearly in the present positron annihilation data. Details of the effect will be discussed elsewhere together with the data of three-dimensional atom probe microscope.

In conclusion, the Cu nanoprecipitation in the RPV steel irradiated in the Calder Hall-type reactor is enhanced by the low dose-rate irradiation (4.2×10^{8} n/cm^2 s) in the very early stage (2.7×10^{17} n/cm^2) and thus prior to eventual formation of matrix defects. On the other hand, in the higher dose-rate irradiation in JMTR (3.6×10^{12} n/cm^2 s), the Cu nanoprecipitation is considerably delayed. The results strongly suggest that the embrittlement caused by Cu nanoprecipitation occurs earlier than seen from accelerated tests in MTRs, so that the accelerated tests are not enough to predict the future embrittlement due to the Cu nanoprecipitation. The present success also suggests that positron annihilation spectroscopy can serve as a unique method for systematic studies of Cu nanoprecipitation in other types of nuclear power reactors, such as boiling water reactors and pressurized water reactors in operation all over the world; those reactors have intermediate irradiation dose rates. Moreover, the positron annihilation technique could be expected to evaluate the recovery of Cu precipitation in RPV steels after in-service annealing as planed in some countries.

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